Reductie en ozonisatie van acetyleenethers

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SUMMARY.

In Chapter I we described the reactions of dialkylaluminiumhydrides $HAl(alk)_2$ with ethoxyethynylcarbinols $R-\underset{R'}{C}(OH)-C\equiv COC_2H_5$. Several products could be isolated depending on the temperature during the hydrolysis of the initial aluminium-containing addition product.

At $-5^{\circ}C$ the diene ethers ($R-\underset{R'}{C}=C=CHOC_2H_5$) could be obtained together with the ethoxyvinylcarbinols. ($R-\underset{R'}{C}(OH)-CH=CHOC_2H_5$).

At $+20^{\circ}C$ a mixture of the cumulated and conjugated diene ethers is formed. These mixtures, which also contain unidentified compounds are difficult to separate.

Only in one instance were we able to obtain a pure conjugated diene ether ($CH_2=\underset{CH_3}{C}-CH=CHOC_2H_5$).

By acid hydrolysis the ethoxyvinylcarbinols as well as the cumulated and conjugated diene ethers are converted into α,β-unsaturated aldehydes.

The reduction of ethoxyethynylcarbinols with dialkylaluminiumhydrides could therefore be used in the synthesis of non-aromatic α,β-unsaturated aldehydes.

$$R-\underset{R'}{C}(OH)-C\equiv COC_2H_5 \xrightarrow[(2)\ \text{hydrolysis at } -5^{\circ} - +20^{\circ}]{(1)\ HAl(alk)_2}$$

$$\left.\begin{array}{l} R-\underset{R'}{C}(OH)-CH=CHOC_2H_5 + \\ +R-\underset{R'}{C}=C=CHOC_2H_5 + \\ +R=\underset{R'}{C}-CH=CHOC_2H_5 \end{array}\right\} \xrightarrow[H^+]{H_2O} R-\underset{R'}{C}=CH-CHO$$

Chapter II deals with the reactions of ozone with unsaturated ethers (vinyl ethers, acetylenic ethers, cumulated diene ethers, ethoxyethynylcarbinols).

It was possible to estimate with this reagent the concentration of the cumulated diene ethers in solution.

On ozonolysis the acetylenic ethers yielded α-keto-esters. This synthesis has some preparative value. The β-hydroxy-α-keto esters, which are not easily accessible, can thus be prepared from the ethoxyethynylcarbinols.